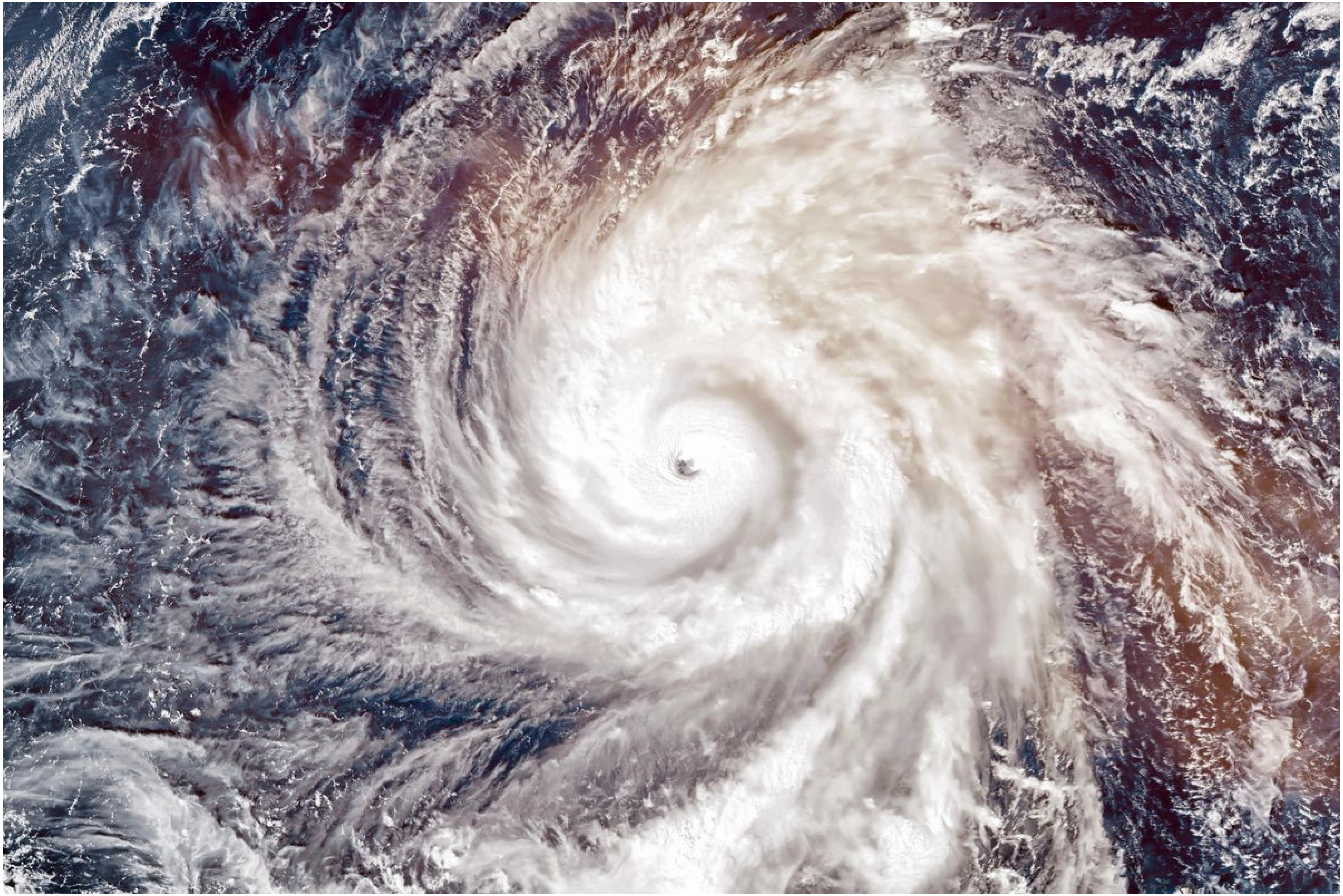
Global stationary thermodynamics

Karol Makuch

Institute of Physical Chemistry PAS

18.11.2022, Penn State

Do thermodynamics-like description beyond equilibrium exist?

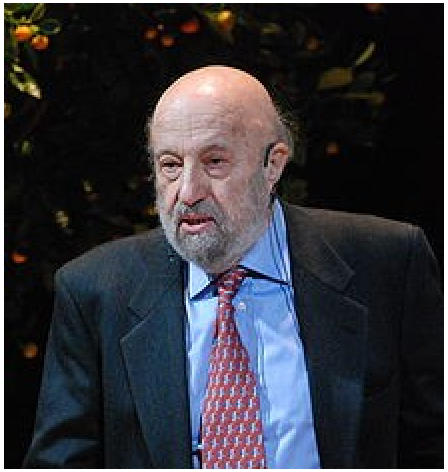


Do thermodynamics-like description beyond equilibrium exist?

The problem is open… started at least around mid XX

`Do there still exist in such situation "thermodynamic potentials" such as the entropy, free energy or entropy production?'

Ilya Prigogine, Introduction to thermodynamics of irreversible processes



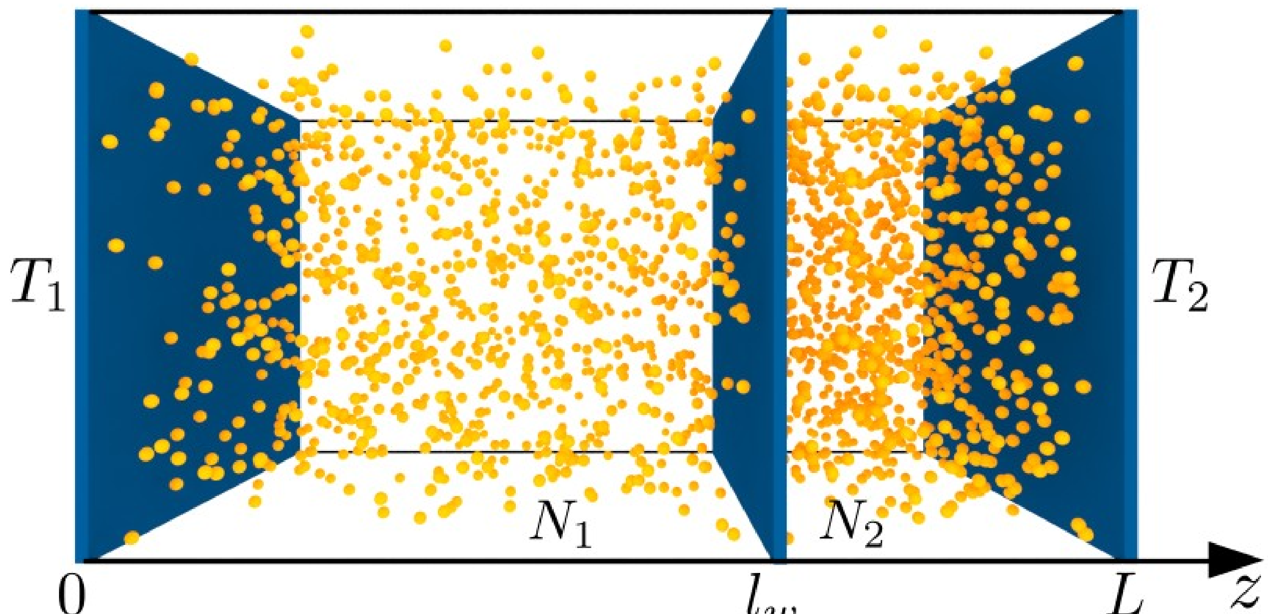
In a nonequilibrium situation, such as the case of a system in contact with two reservoirs, we may expect a more complex entanglement between the variables describing the system and those related to the environment, so that it is unlikely that quantities such as U, S, . . . can be simply defined.

Giovanni Jona-Lasinio J. Stat. Mech. (2014) P02004

Thermodynamics: Callen's perspective

`The single, all-encompassing problem of thermodynamics is the determination of the equilibrium state that eventually results after the removal of internal constraints in a closed, composite system'

Callen. "Thermodynamics and an Introduction to Thermostatistics"



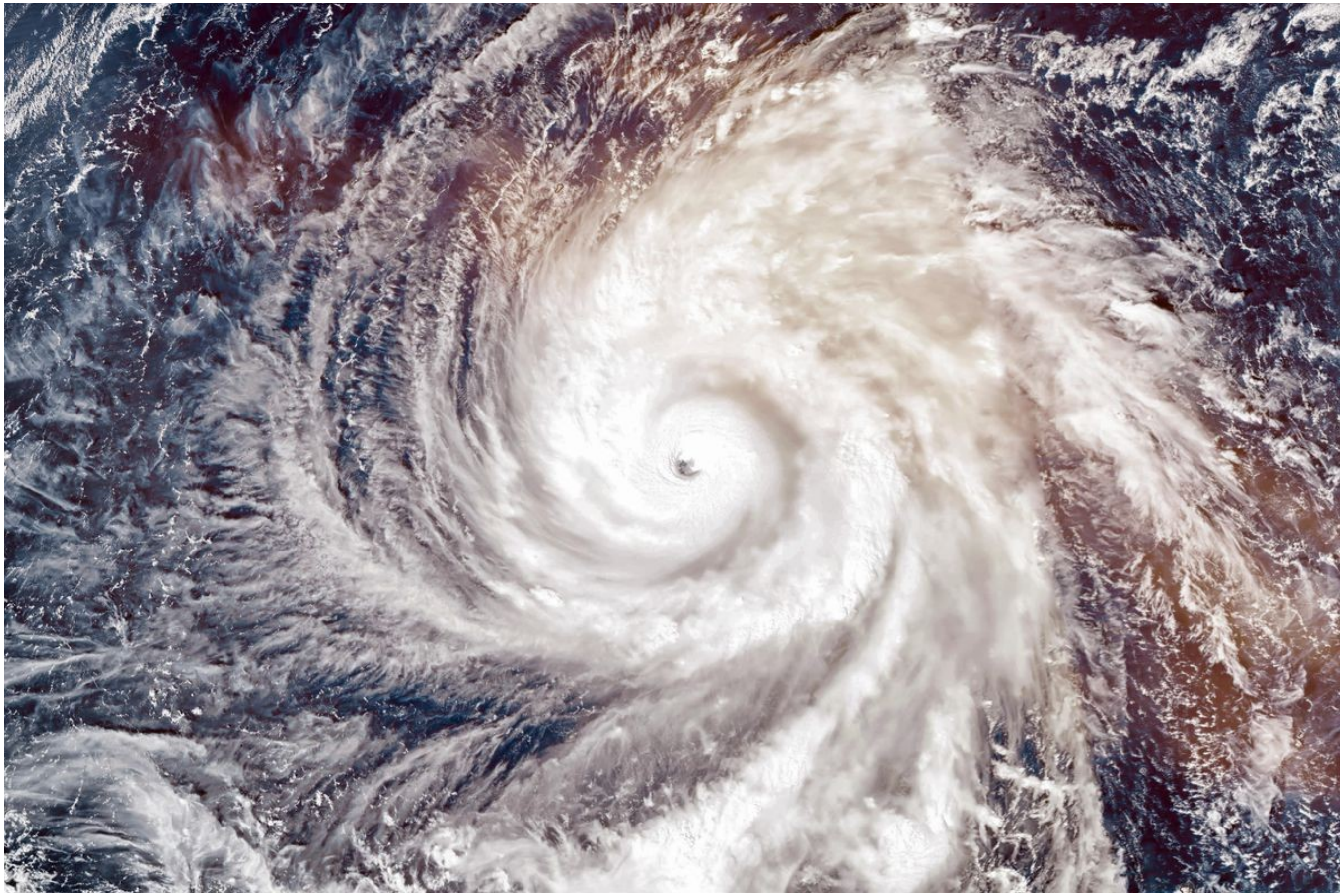
Thermodynamics: zero, first, second law

0 equality of temperatures at contact

1 energy balance

2 existence of additive entropy,
maximum entropy principle
(minimum energy principle)

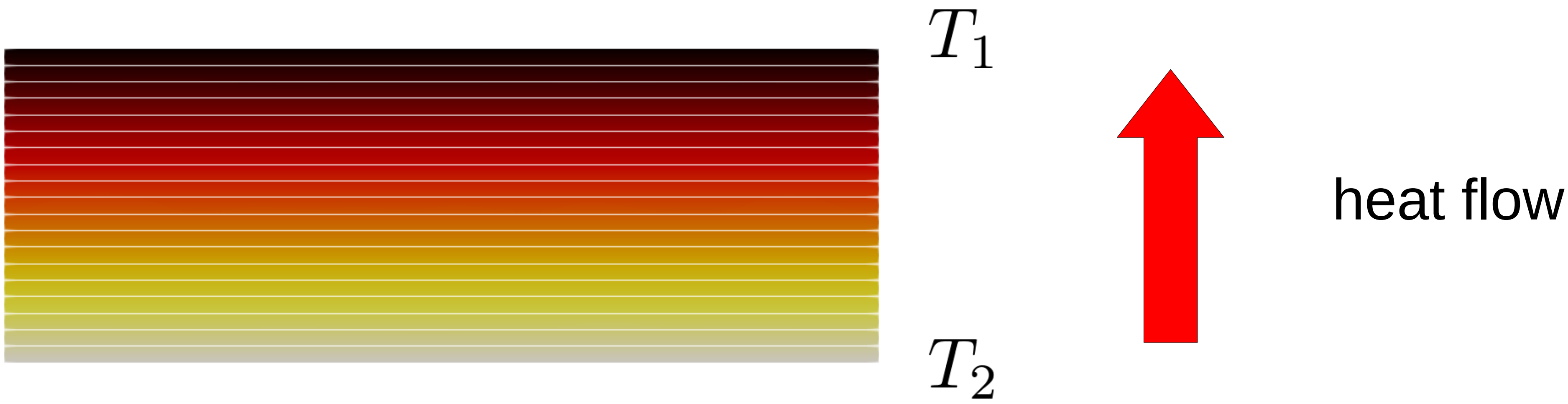
Do global stationary thermodynamics exist?



heat <=> work (expansion) <=> kinetic energy (wind)

beyond equilibrium (e.g. in heat flow)

Simplest system: ideal gas in a heat flow



DYNAMICS GOVERNED BY [de Groot, Mazur]:

- Two equations of state
- Mass conservation equation
- Momentum balance equation
- Energy balance equation

+ Fourier law with constant heat conductivity coefficient

Main idea of the approach

Robert Hołyst

The new theory must directly reduce to equilibrium formulation. → e.g. a function that reduces to entropy...

ME

… so we need to rebuild thermodynamics by generalizing thermodynamic notions to the nonequilibrium situation

Where to start?

entropy

temperature

integrating factor

heat

constaints

Helmholtz free energy

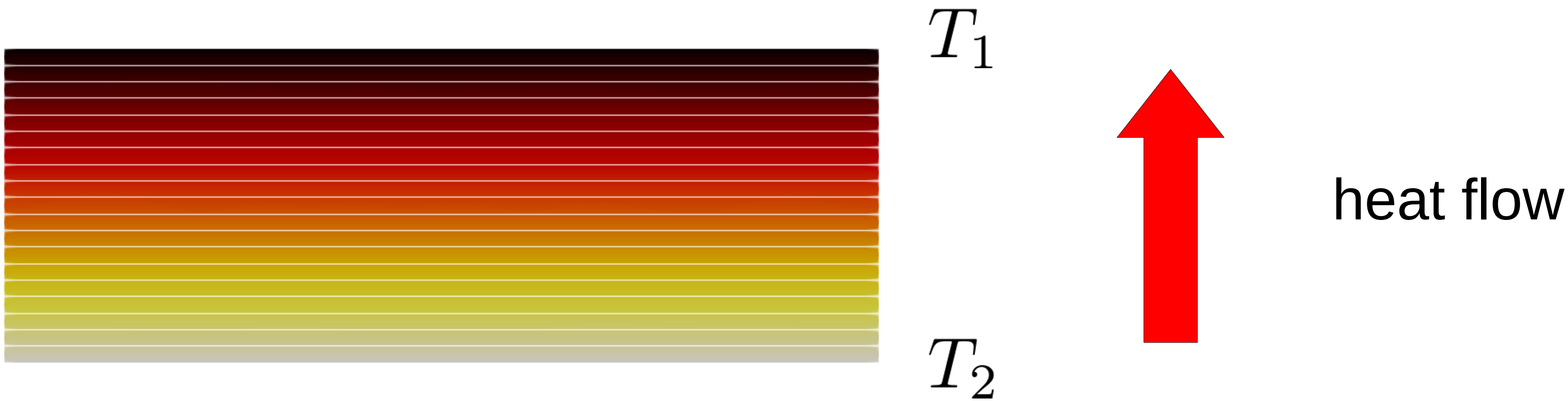
work

quasistatic process

heat differential

Oono and Paniconi, Progress of Theoretical Physics Supplement, 130:2944, 1998

Simplest system: ideal gas in a heat flow



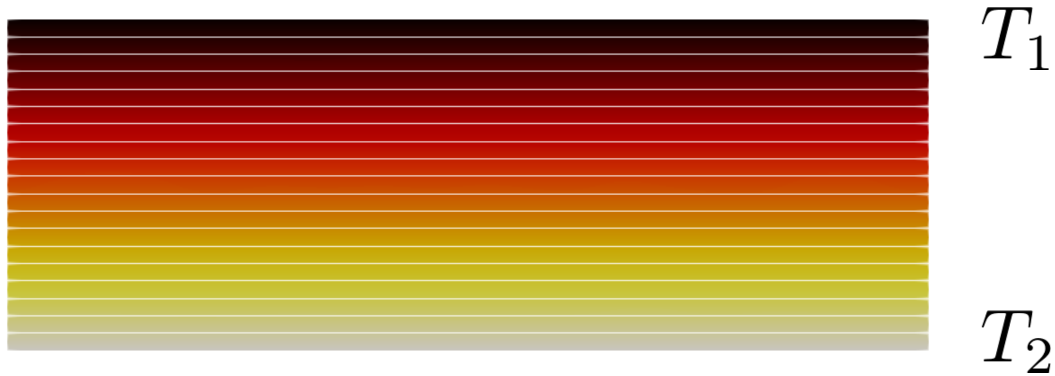
$$T\left(z\right) = T_1 + \left(T_2 - T_1\right)\frac{z}{L}$$

$$U = \frac{3}{2} N k_B \frac{T_2 - T_1}{\log \frac{T_2}{T_1}}$$

$$p(U, V, N, T_2/T_1) = \frac{2}{3}\frac{U}{V}$$

as in equilibrium

Energy balance and change of stationary state



$$T_2 \rightarrow T_2'$$

times: t_i t_f

de Groot, Mazur:

and where

$$\rho \frac{\mathrm{d}q}{\mathrm{d}t} = -\operatorname{div} \boldsymbol{J}_q \tag{38}$$

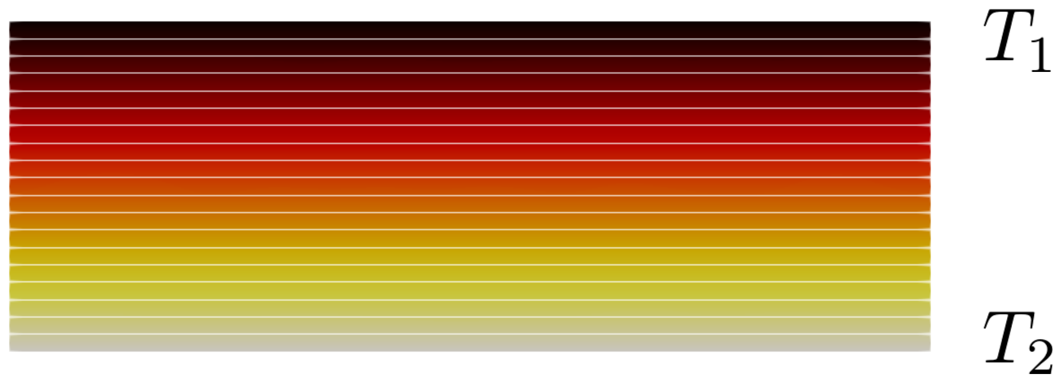
defines dq, the "heat" added per unit of mass.

With (14) equation (36), the "first law of thermodynamics", can finally be written in the form

$$\frac{\mathrm{d}u}{\mathrm{d}t} = \frac{\mathrm{d}q}{\mathrm{d}t} - p\frac{\mathrm{d}v}{\mathrm{d}t} - v\Pi : \mathrm{Grad}\, \boldsymbol{v} + v \sum_k \boldsymbol{J}_k \cdot \boldsymbol{F}_k\,, \tag{39}$$

where $v \equiv \rho^{-1}$ is the specific volume.

Starting point – net heat and first law of GST



$$T_2 \rightarrow T_2'$$

times: t_i t_f

hydrodynamics :

1! $$\Delta U_{t_f t_i} = Q_{t_f t_i} + W_{t_f t_i} \qquad dU = \text{đ}Q + \text{đ}W$$

slow (quasisteady) change:

$$\text{đ}W_{t_f t_i} = -p dV$$

Integrating factor and potential (nonequlibrium entropy)

$$đQ = dU + pdV$$

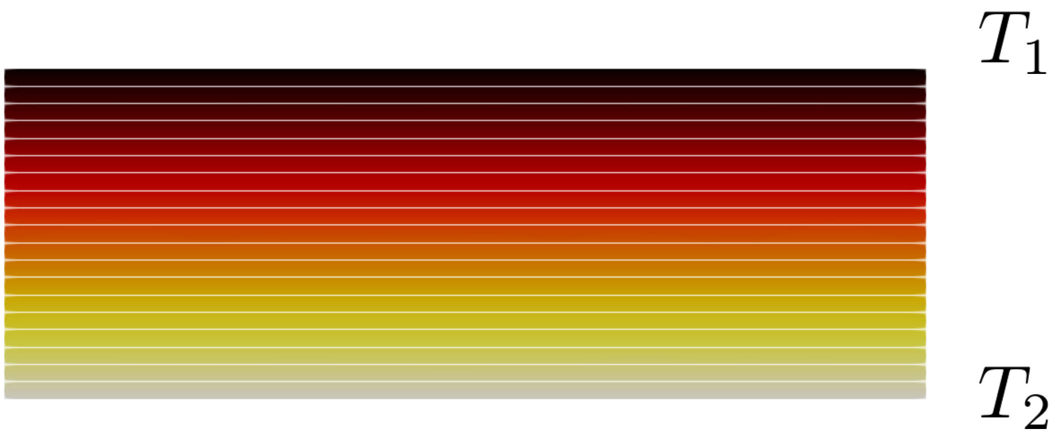
As in equilibrium, we look for a function that determine steady-adiabatic (no net heat exchange) surface:

$$S^*(U, V, N, T_2/T_1) = S_0$$

$$dS^* \equiv \frac{đQ}{T^*}$$

integrating factor

Nonequilibrium entropy exists for ideal gas



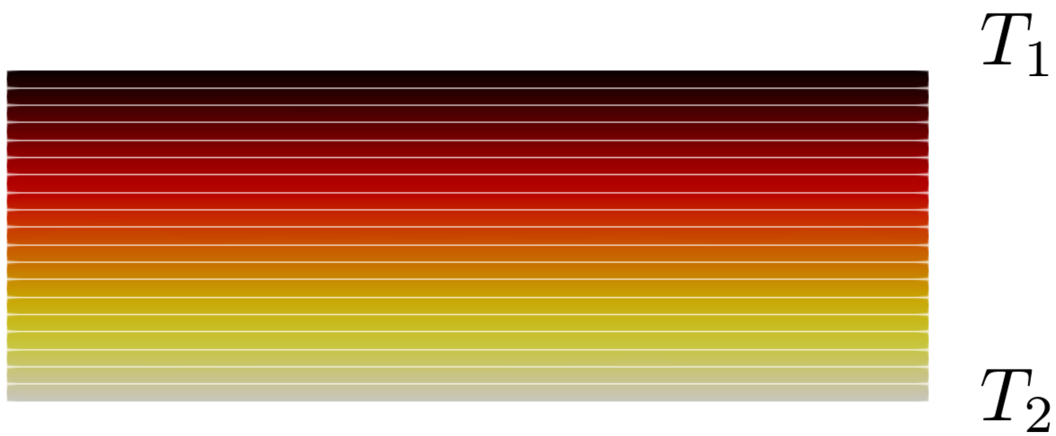
$$\text{đ}Q = T^* dS^*$$

$$T^* = \frac{2U}{3Nk_B}$$

a num. constant

$$S^*(\underline{U}, V, N, \underline{T_2/T_1}) = Nk_B \left\{ \frac{5}{2} + \frac{3}{2} \log \left[\frac{2}{3} \frac{\varphi_0 U}{N} \left(\frac{V}{N} \right)^{2/3} \right] \right\}$$

Nonequilibrium entropy vs total eq. entropy



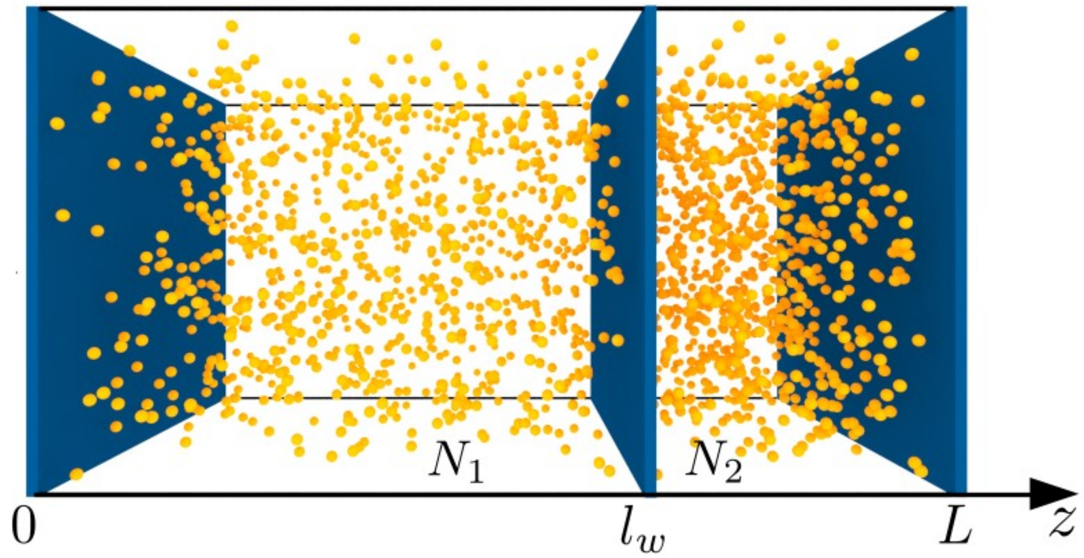
$$S = S^* + \Delta S$$

total eq. entropy
(integrated over volume)

noneq. entropy

$$\Delta S = N k_B \log \left[\left(\frac{T_2}{T_1} \right)^{5/4} \left(\frac{\log \frac{T_2}{T_1}}{\frac{T_2}{T_1} - 1} \right)^{5/2} \right]$$

Second law of thermodynamics



$$\min_{S_1, V_1} \left[U_1 \left(S_1, V_1, N_1 \right) + U_2 \left(S_2, V_2, N_2 \right) \right]$$

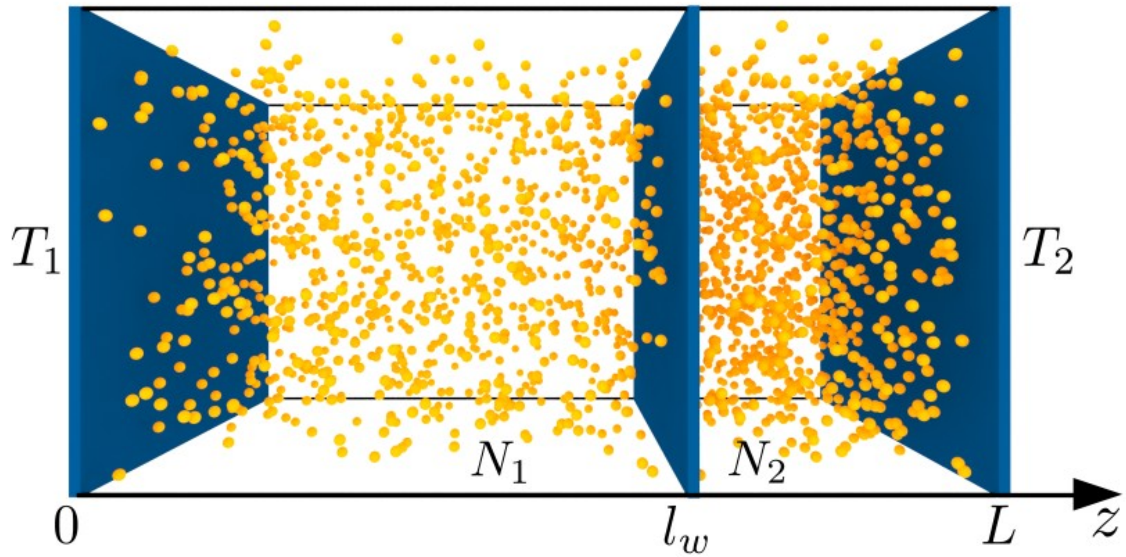
$$V = V_1 + V_2 \qquad S_{12} = S_1 + S_2$$

$$T_1 = T_2$$ ← *zeroth law*

$$p_1 = p_2$$ ← *mechanical equilibrium*

Second law of global stationary thermodynamics

Makuch, Hołyst. Maciołek, Żuk, J. Chem. Phys. 157, 194108 (2022)



$$\min_{S_1^*, V_1} \left[U_1\left(S_1^*, V_1, N_1\right) + U_2\left(S_2^*, V_2, N_2\right)\right]$$

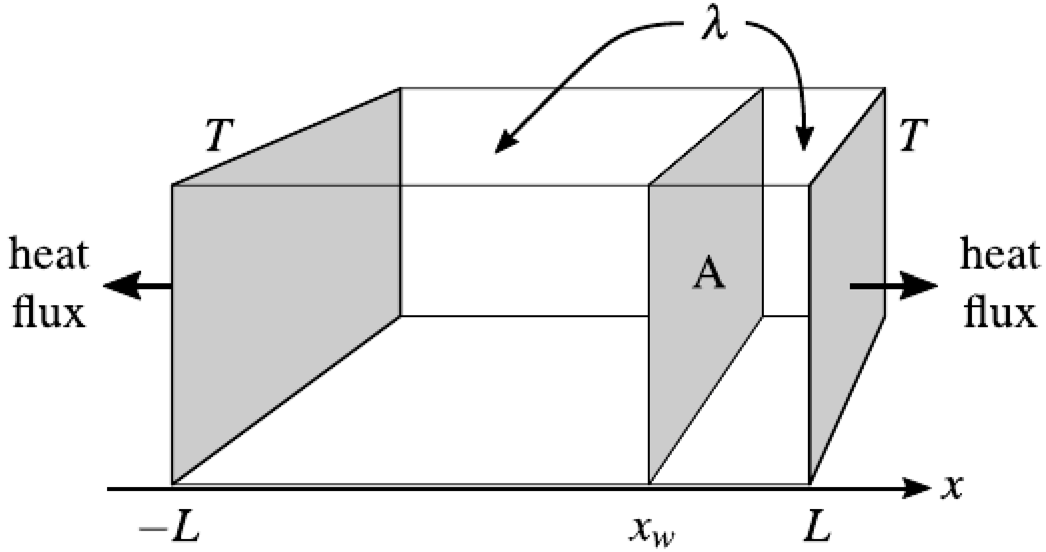
$$V = V_1 + V_2 \qquad S_{12}^* \equiv S_1^* + rS_2^*$$

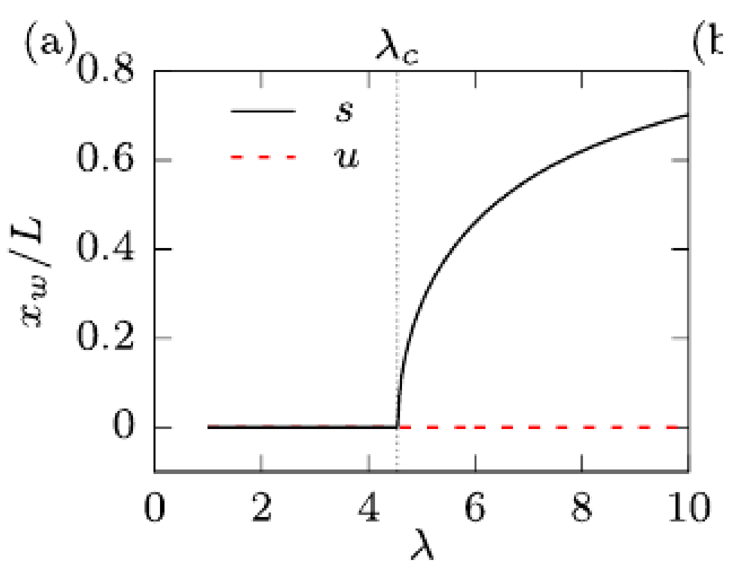
$$rT_1^* = T_2^*$$ ← *"zeroth law condition"*

$$p_1 = p_2$$ ← *mechanical equilibrium*

Equilibrium for $r \to 1$.

Applications: ideal gas with volumetric heating and phase transition





Zhang, Litniewski, Makuch, Zuk, Maciołek, Hołyst. Phys. Rev. E, 104:024102 (2021)

position of the wall given by the second law of global stationary thermodynamics

Applications: beyond linear irreversible thermodynamics

Linear Fourier law:

$$J_{heat} = -\kappa \nabla T$$

state determined by the minimum entropy production principle

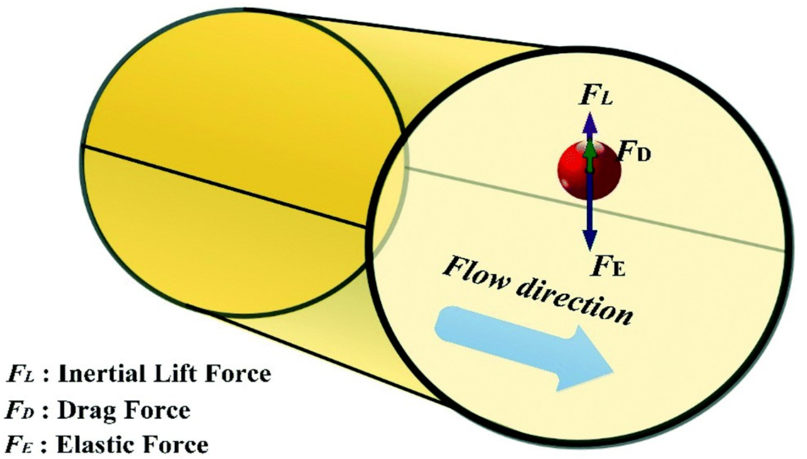
Nonlinear Fourier law:

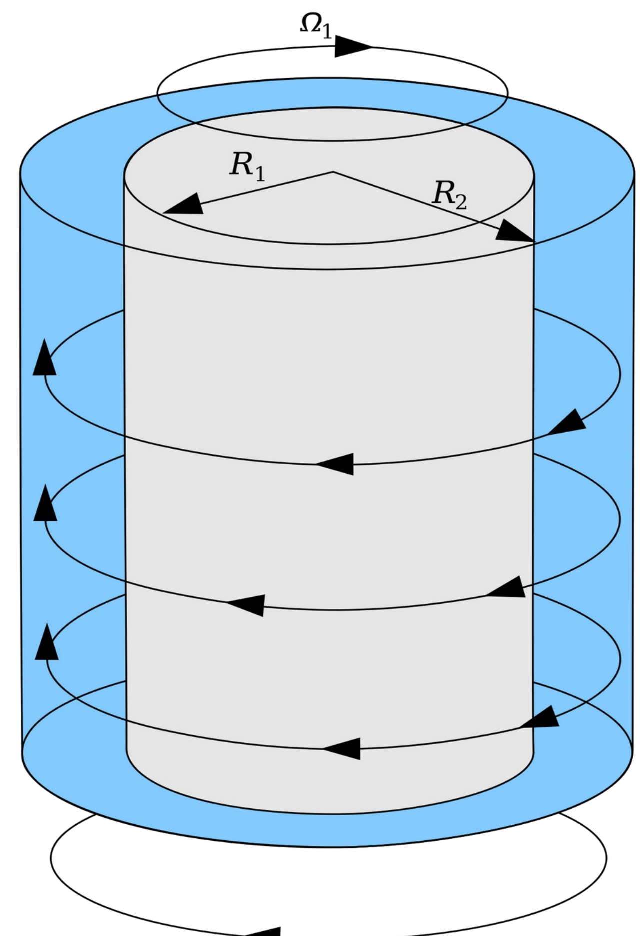
$$J_{heat} = -\kappa(T) \nabla T$$

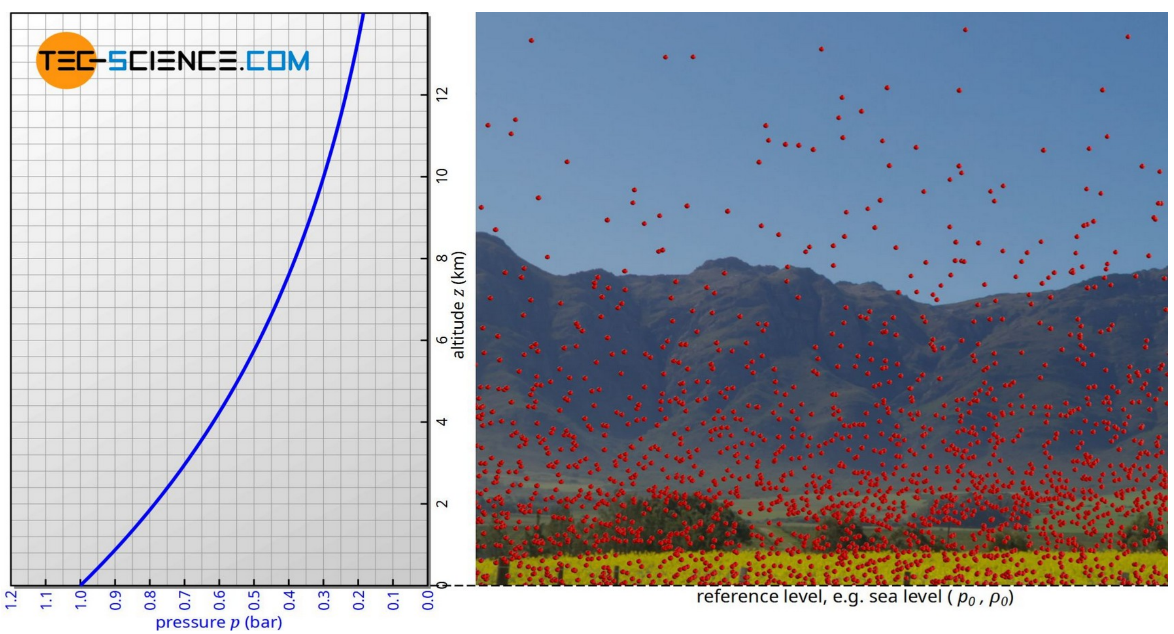
nonlinearity breaks the minimum entropy production principle

position of the wall given by the second law of global stationary thermodynamics

Outlook: interactions, kinetic energy, external field, chemical reactions







Mixture of Gases A and B